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OXIDATION OF AMMONIA

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MICROMEDIA

OXIDATION OF AMMONIA - LITERATURE SURVEY

by

K.E. Haque*

ABSTRACT

This limited literature survey provides a brief account of oxidative decomposition of ammonia or ammonium salts with O_2 , O_3 , H_2O_2 , Cl_2 and SO_2-O_2 . The decompositions of ammonia and ammonium salts by electrooxidation, photolysis and chemical treatment have also been included.

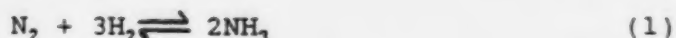
The processes of electrooxidation, oxidation with hypohalite (OCl^- , OBr^-) and the breakpoint chlorination oxidize ammonium salts into nitrogen and water; whereas oxidation with peroxide, persalts and catalyzed by metal oxide lead to the formation of nitrate and nitrite. However, nitrogen evolves when an ammonium salt is treated with a nitrite. The pros and cons of these oxidation processes have been discussed and the recommendation for further R and D investigations have been put forward.

Keywords: Ammonia, Ammonia Oxidation, Ammonia Decomposition

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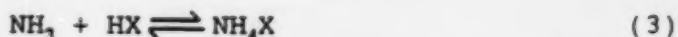
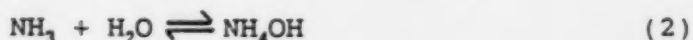
INTRODUCTION

Ammonia is an important industrial chemical and always present in air and natural water in trace amounts. Industrially it is synthesized from gaseous nitrogen and hydrogen at high temperatures, under pressure and in the presence of a catalyst (eq. 1) (1).



The occurrence of ammonia gas and/or ammonium salts in a mine mill operation is a common phenomenon. The majority of the ammonia in the mine mill operations is generated from the chemicals applied in the explosive devices, through oxidation and hydrolysis of cyanides in gold mills and ammonium salts utilized in yellow cake precipitation in some uranium mills.

Ammonia is a moderately strong base, reacts with water and vigorously with acids (eq. 2 and 3); but it also undergoes oxidation, decomposition, complexation with different metals salts and adsorption on many inert materials. This preliminary review provides a very brief account of the oxidation of ammonia in aqueous medium with some common oxidants; such as O_2 (g), O_3 , Cl_2 , peroxides and SO_2 - O_2 mixture.

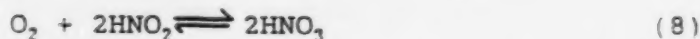
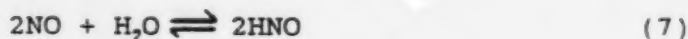
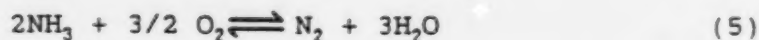


(X = Cl, Br, NO_3 , etc.)

Oxidation with Oxygen

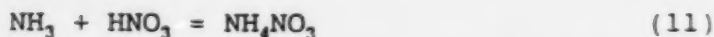
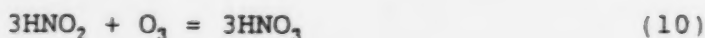
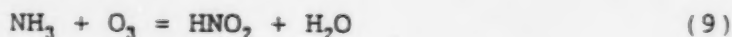
Ammonia gas burns in air or oxygen with the formation of nitrogen, steam and some oxides of nitrogen (1,2,6,7). However, ammonia (g) undergoes oxidation with oxygen (air or oxygen) at high temperatures and in the presence of a metal catalyst

(e.g., Pt, Pt-Ir or Pt-Rh) or metal oxide (e.g., MnO_2) generally with the formation of nitric oxide and steam (eq. 5-8). However, there is no report in the literature on the oxidation of ammonium salts in aqueous medium with air or gaseous oxygen.



Oxidation with Ozone

Ozone is a more powerful oxidant than molecular oxygen (air or oxygen gas). Generally dry ozone does not react with dry ammonia under ordinary condition of temperature and pressure; however, in the presence of moisture ozone oxidizes ammonia into ammonium nitrate (eq. 9-11) (2).



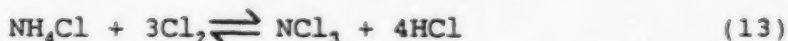
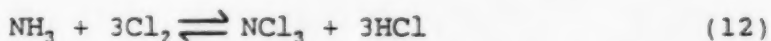
It is reported in the literature that the oxidation of ammonia or its salt in the aqueous medium is considerably accelerated with the presence of bromide anion (3) and also by catalyst (4,5).

Oxidation with Peroxides

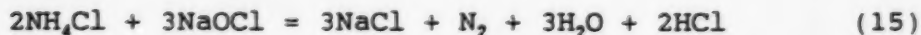
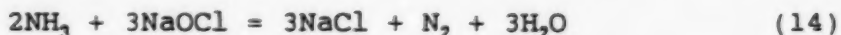
Reports are available in the literature on the oxidation of ammonia or ammonium salts with H_2O_2 , metal oxide (e.g., PbO_2 , Co_2O_3 , MnO_2 , Fe_2O_3 , etc.), persalts (e.g., KMnO_4 , $\text{K}_2\text{S}_2\text{O}_8$). Generally the principal oxidation products are the nitrite and nitrate salts of ammonia (2,6).

Oxidation with Halogen

Gaseous ammonia burns in chlorine with the formation of nitrogen trichloride which is explosive. Even ammonium salts react with chlorine gas (dry reaction) and form nitrogen trichloride (eq. 12, 13) (2,7).



Pressley et al. (8,9) invented the breakpoint chlorination process for the decomposition of dissolved ammonia from waste water. However, when ammonia or ammonium salts are treated with hypochlorite or hypobromite of sodium or calcium, nitrogen gas evolves (eq. 14, 15) (2,10).



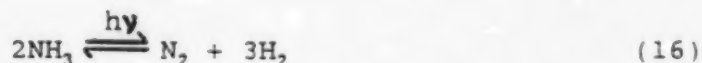
Electrooxidation

An aqueous solution of ammonia or an ammonium salt can be oxidized anodically into elemental nitrogen (2). Reports in the recent literature indicate that anodic oxidation of ammonia can happen even at the concentration of 1-2 mg/L ammonia in solution by using platinum electrode. However, no nitrate (NO_3^-), nitrite (NO_2^-), hydrazine (N_2H_4) or hydroxyl amine (NH_2OH) was detected in the product mixture (2,11,12). Evidently, electrooxidation of

ammonia has technological merits except for the economic (high capital cost, especially for the electrode). However, under the present circumstances it may be logical to conduct some R and D investigations for the development of a cost-effective electrode.

Photolysis of Ammonia

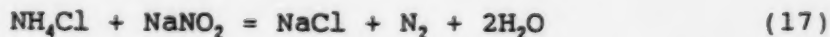
Ultraviolet light can decompose ammonia into nitrogen and hydrogen (eq. 16) (1). It is also reported in the literature that ammonium nitrate was formed when a mixture of ammonia and oxygen (air or O_2 (g)) was exposed to bright, hot sunlight (2). Nitrate and/or nitrite formation also takes place when ammonia or ammonium salt is treated with hypochlorite in the presence of UV light (10).



A mixture of sulphur dioxide (SO_2) and oxygen is finding increasing application in the oxidation of cyanides in the gold mill effluents. Generally, cyanide oxidation is accelerated with the presence of copper (Cu^{+2}) in the reaction mixture. As an oxidant this mixture is comparable with H_2O_2 ; however, there is hardly any report in the literature on oxidation of ammonia with this mixture. Under the present circumstances some R and D investigations are necessary for the evaluation of its feasibility of oxidation of ammonia or ammonium cation.

Chemical Decomposition

It is well documented in the literature that ammonia or ammonium salts can be decomposed into nitrogen by treating with a solution of nitrite (7) (eq. 17).



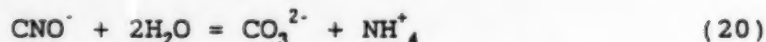
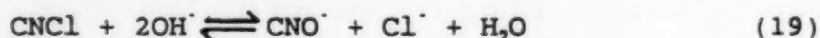
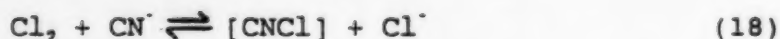
Evidently, this process has considerable technological significance but its economics and potential environmental effects from the soluble nitrite are yet to be studied.

Comments and Recommendations

An oxidation process which leads to the decomposition of ammonia or ammonium salts into nitrogen and hydrogen or nitrogen and water would be the most desirable one. In this respect, processes of electrooxidation, breakpoint chlorination, and oxidation with hypochlorite or hypobromite of ammonia or ammonium salts are notable. The principal discouraging factors for the electrooxidation process are the capital costs especially with respect to electrode materials (Pt). As it appears now, some R and D (in-house or contracting out) investigations may be necessary for the development of a cost-effective electrode. However, it would be prudent to make preliminary cost estimates for the process with the conventional electrode (i.e., Pt) as well as with the electrodes made of inexpensive materials.

Breakpoint chlorination and hypochlorite or hypobromite oxidation of ammonia or ammonium salts essentially follow the same reaction mechanism. In fact gold mill operations have been utilizing hypochlorite for the oxidation of cyanides in the mill effluents. However, the operation is conducted by sparging chlorine gas through the effluents under alkaline condition (essentially with no knowledge in OCl^- concentration).

It is generally believed that the oxidation of cyanide (CN^-) into cyanate (CNO^-) takes place through the formation of the intermediate; cyanogen chloride (CNCl) followed by hydrolysis into cyanate (CNO^-) (eq. 18, 19). Ammonia is formed through hydrolysis of cyanate (eq. 20). If sufficient hypochlorite (OCl^-) would have been present in the reaction mixture the oxidation of N^+H_4 might follow according to eq. 15. Obviously some R and D investigations are necessary in order to utilize this process for the abatement of ammonia in the gold mill effluents.



Photochemically ammonia can be decomposed into nitrogen and hydrogen; but this process needs considerable amount of R and D investigations in order to establish its technological feasibility. It is doubtful that this process would be at all economically viable.

The oxidation of ammonia with ozone, hydrogen peroxide, heavy metal oxides or persalts are scientifically feasible but the economics remain questionable. A number of gold mills are applying hydrogen peroxide treatment process for the oxidation of cyanides in the mill effluents but often without being successful in controlling of ammonia problem in the final discharge. It is generally believed that cyanate (CNO^-) is the principal oxidation product of cyanide with hydrogen peroxide. Most probably ammonia evolution could be avoided by extending the oxidation beyond cyanate formation. In fact some R and D investigations are essential to study the feasibility of cyanide oxidation.

The process of nitrite decomposition of ammonium salts has considerable technological significance; but further R and D investigations are necessary to evaluate its economic feasibility.

A number of inorganic chemicals such as acids, CaCl_2 , CaBr_2 , FeCl_2 , MnCl_2 , CuSO_4 , NH_4NO_3 , respectively absorb ammonia gas (7). This absorption phenomenon may be utilized for the removal of ammonia gas from the fouled air in the mine-mill environment (e.g., by developing a suitable scrubber). Extensive R and D investigations are necessary to evaluate its technological and economic feasibilities.

Adsorption-decomposition mechanism may be applied for the removal of ammonium cations from the mill effluents by adsorption

on a cation exchanger followed by decomposition into nitrogen (N_2) with nitrite treatment. This concept needs extensive R and D investigations to evaluate its technological and economic feasibilities.

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